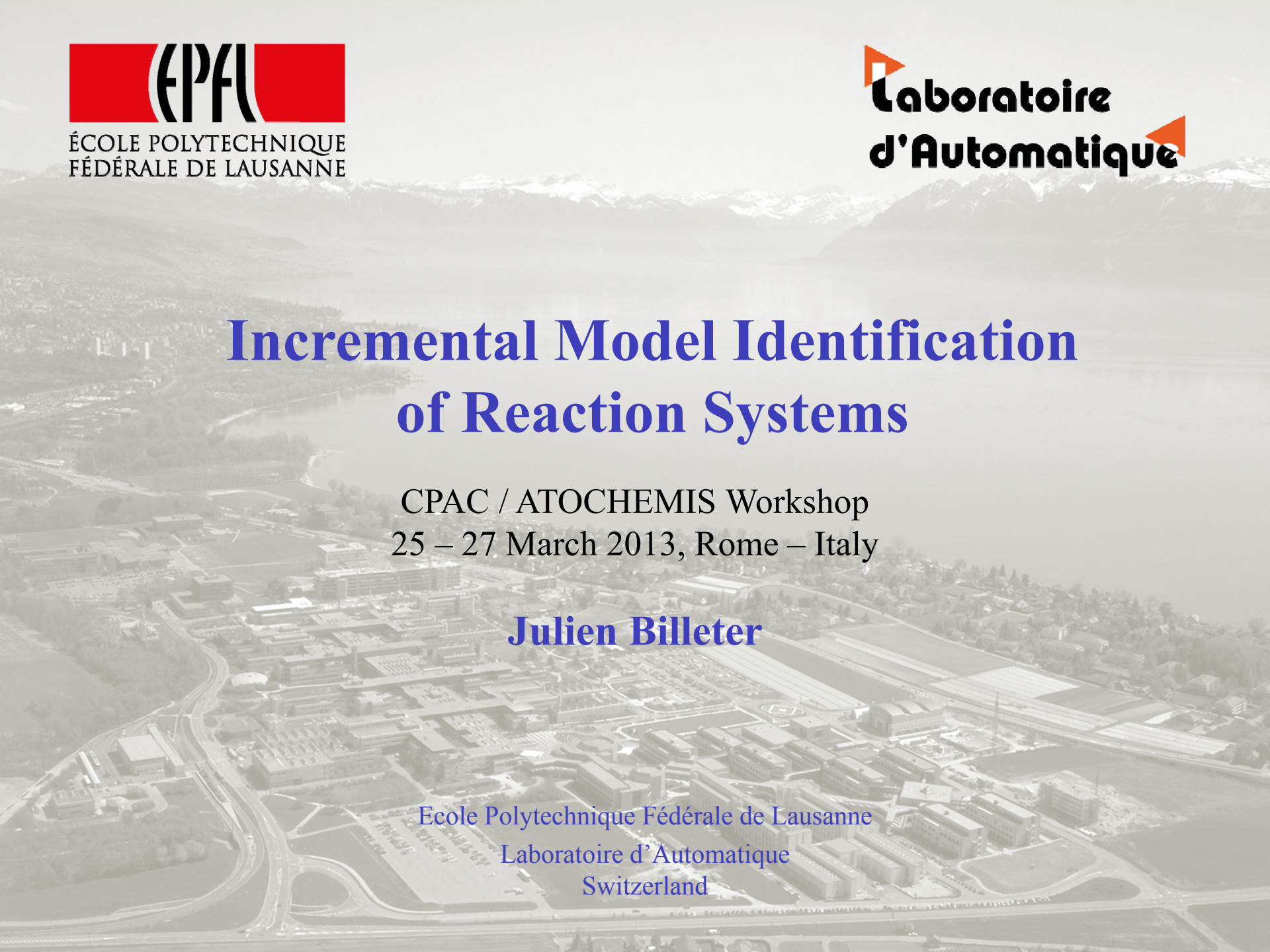

Incremental Model Identification of Reaction Systems

CPAC / ATOCHEMIS Workshop
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Outline

- Motivation
- Concept of vessel extent
- Homogeneous reaction systems
- Incremental model identification
- Fluid-Fluid reaction systems
- Extensions to calorimetry and spectroscopy
- Perspectives: distributed reaction systems

Model reduction
Separate fast / slow dynamics

- Discard redundant (invariant) states
  - What is the minimal number of states (variants) ?
  - Batch reactors: $S \rightarrow R$ extents
  - Open reactors: $S \rightarrow R+p+1$ *vessel* extents
  - Open G-L reactors: $S \rightarrow R+p_m+p+1$ *vessel* extents
- Separate fast/slow dynamics
  - Rates are fast/slow, not individual concentrations

  → work with extents, not concentrations…

Bhatt et al, Comp. & Chem. Eng. (2011), submitted
M. Amrhein, PhD dissertation n°1861 (1998), EPFL, Switzerland

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Definitions
Extent vs vessel extent of reaction

- Extent of the *i*-th reaction $\xi_{r,i}(t)$:
  number of moles produced by the *i*-th reaction

Differential extent of reaction

$$\dot{\xi}_{r,i}(t) = \frac{1}{\nu_{s,i}} \dot{n}_s = r_{v,i}(t) \qquad \xi_{r,i}(0) = 0$$

- Vessel extent of the *i*-th reaction $x_{r,i}(t)$:
  number of moles produced by the *i*-th reaction still in vessel

Differential vessel extent of reaction

$$\dot{x}_{r,i}(t) = r_{v,i}(t) - \frac{u_{out}(t)}{m(t)} x_{r,i}(t) \qquad x_{r,i}(0) = 0$$

Definitions
Extent vs vessel extent of mass transfer

- Extent of the *j*-th mass transfer $\xi_{m,j}(t)$:
  mass transferred by the *j*-th mass transfer

Differential extent of mass transfer

$$\dot{\xi}_{m,j}(t) = \zeta_j(t) \qquad \xi_{m,j}(0) = 0$$

- Vessel extent of the *j*-th mass transfer $x_{m,j}(t)$:
  mass transferred by the *j*-th mass transfer still in vessel

Differential vessel extent of mass transfer

$$\dot{x}_{m,j}(t) = \zeta_j(t) - \frac{u_{out}(t)}{m(t)} x_{m,j}(t) \qquad x_{m,j}(0) = 0$$

General concept of vessel extent

A vessel extent indicates the amount of material (number of moles, mass, volume), associated with one phenomenon, that is still in the vessel…

Differential vessel extent (i-th phenomenon f)

$$\dot{x}_{f,i}(t) = \dot{\xi}_{f,i}(t) - \frac{u_{out}(t)}{m(t)} x_{f,i}(t) \qquad x_{f,i}(0) = 0$$

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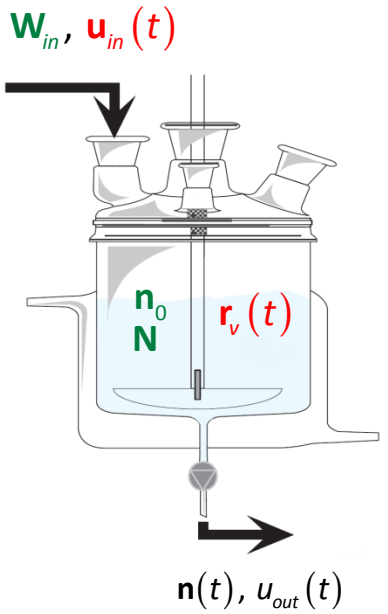
Homogeneous reaction systems
Mole balance equations

Homogeneous reaction system consisting of S species, R independent reactions, p independent inlets and one outlet

Mole balances for S species

$$\underset{(S\times 1)}{\dot{\mathbf{n}}(t)} = \underset{(S\times R)\ (R\times 1)}{\mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t)} + \underset{(S\times p)\ (p\times 1)}{\mathbf{W}_{in}\mathbf{u}_{in}(t)} - \frac{u_{out}(t)}{m(t)}\mathbf{n}(t),\quad \underset{(S\times 1)}{\mathbf{n}(0)} = \mathbf{n}_0$$



Mass, volume and concentrations

$$\mathbf{m}(t) = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t),\quad V(t) = \frac{m(t)}{\rho(t)},\quad \mathbf{c}(t) = \frac{\mathbf{n}(t)}{V(t)}$$

Homogeneous reaction systems
Decomposition in variants and invariants

- Condition: $\operatorname{rank}\left(\left[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{in}\ \mathbf{n}_0\right]\right) = R + p + 1$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} \overset{\mathscr{L}}{=} \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{q}^{\mathrm{T}} \\ \mathbf{Q} \end{bmatrix} \left(\mathbf{n}(t) - \mathbf{n}_0\right)$$

- Vessel extents (variants) and $q = S - R - p - 1$ redundant information (invariants)

$$\dot{\mathbf{x}}_r(t) = \underbrace{\mathbf{R}\,\mathbf{N}^{\mathrm{T}}}_{\mathbf{I}_R}\mathbf{r}_v(t) + \underbrace{\mathbf{R}\,\mathbf{W}_{in}}_{\mathbf{0}_{R\times p}}\mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R$$

$$\dot{\mathbf{x}}_{in}(t) = \underbrace{\mathbf{F}\,\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}_{p\times R}}\mathbf{r}_v(t) + \underbrace{\mathbf{F}\,\mathbf{W}_{in}}_{\mathbf{I}_p}\mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p$$

$$\dot{x}_{ic}(t) = \underbrace{\mathbf{q}^{\mathrm{T}}\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}_{1\times R}}\mathbf{r}_v(t) + \underbrace{\mathbf{q}^{\mathrm{T}}\mathbf{W}_{in}}_{\mathbf{0}_{1\times p}}\mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\left(1 + x_{ic}(t)\right), \qquad x_{ic}(0) = 0$$

$$\dot{\mathbf{x}}_{iv}(t) = \underbrace{\mathbf{Q}\,\mathbf{N}^{\mathrm{T}}}_{\mathbf{0}_{q\times R}}\mathbf{r}_v(t) + \underbrace{\mathbf{Q}\,\mathbf{W}_{in}}_{\mathbf{0}_{q\times p}}\mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\dot{\mathbf{x}}_{iv}(t), \qquad \mathbf{x}_{iv}(0) = \mathbf{0}_q$$

Homogeneous reaction systems
Decomposition in variants and invariants

- Condition: $\operatorname{rank}\left(\left[\mathbf{N}^{\mathrm{T}} \;\; \mathbf{W}_{in} \;\; \mathbf{n}_0\right]\right) = R + p + 1$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} \overset{\mathscr{L}}{=} \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{q}^{\mathrm{T}} \\ \mathbf{Q} \end{bmatrix} \left(\mathbf{n}(t) - \mathbf{n}_0\right)$$

- Vessel extents (variants) and $q = S - R - p - 1$ redundant information (invariants)

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \frac{u_{out}(t)}{m(t)}\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \frac{u_{out}(t)}{m(t)}\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p$$

$$\dot{x}_{ic}(t) = -\frac{u_{out}(t)}{m(t)} - \frac{u_{out}(t)}{m(t)}x_{ic}(t), \qquad x_{ic}(0) = 0$$

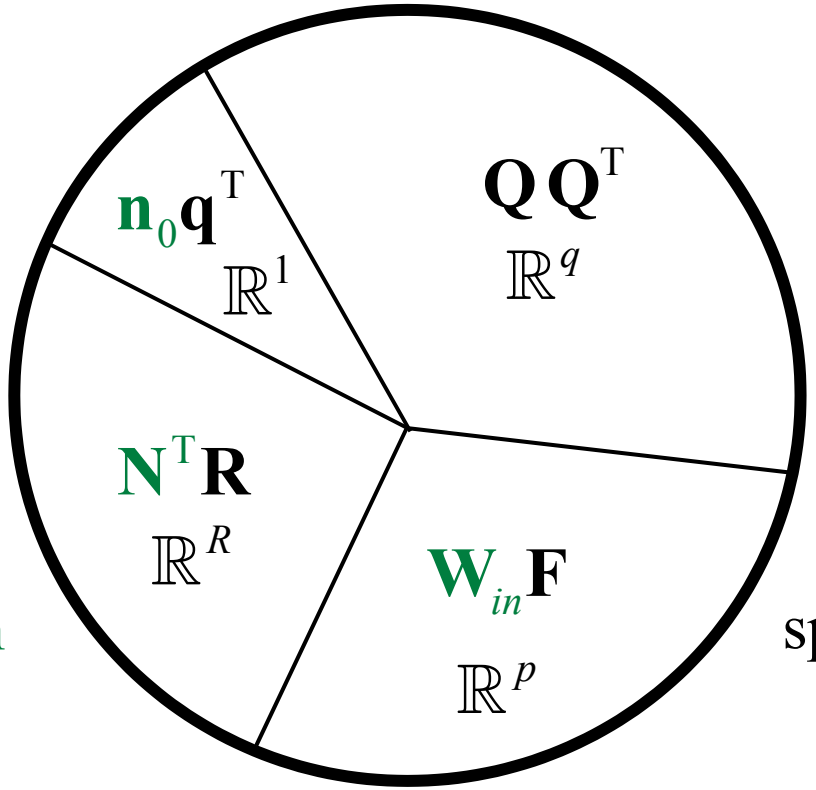
$$\mathbf{x}_{iv}(t) = \mathbf{0}_q$$

- Reconstruction: $\left(\mathbf{n}(t) - \mathbf{n}_0\right) \overset{\mathscr{L}^{-1}}{=} \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t)$

Homogeneous reaction systems
Orthogonal spaces in 4-way decomposition

space of initial conditions

space of invariants



space of reaction extents

space of inlet extents

***S*-dim space of the number of moles**

Homogeneous reaction systems
Transformation to RV form

- When $\text{rank}\left(\left[\mathbf{N}^{\mathrm{T}}\ \mathbf{W}_{in}\ \mathbf{n}_0\right]\right) < R + p + 1$ $\left(\mathbf{u}_{in}(t)\text{ and }u_{out}(t)\text{ known}\right)$, the numbers of moles are rearranged in **R**eaction **V**ariant (RV) form:

$$\mathbf{n}^{\mathrm{RV}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) = \mathbf{n}(t) - \mathbf{W}_{in}\mathbf{x}_{in}(t) - \mathbf{n}_0\left(1 + x_{ic}(t)\right)$$

- The R **vessel extents of reaction** are then computed as:

$$\mathbf{x}_r(t) = \left(\mathbf{N}^{\mathrm{T}}\right)^{+}\mathbf{n}^{\mathrm{RV}}(t)$$

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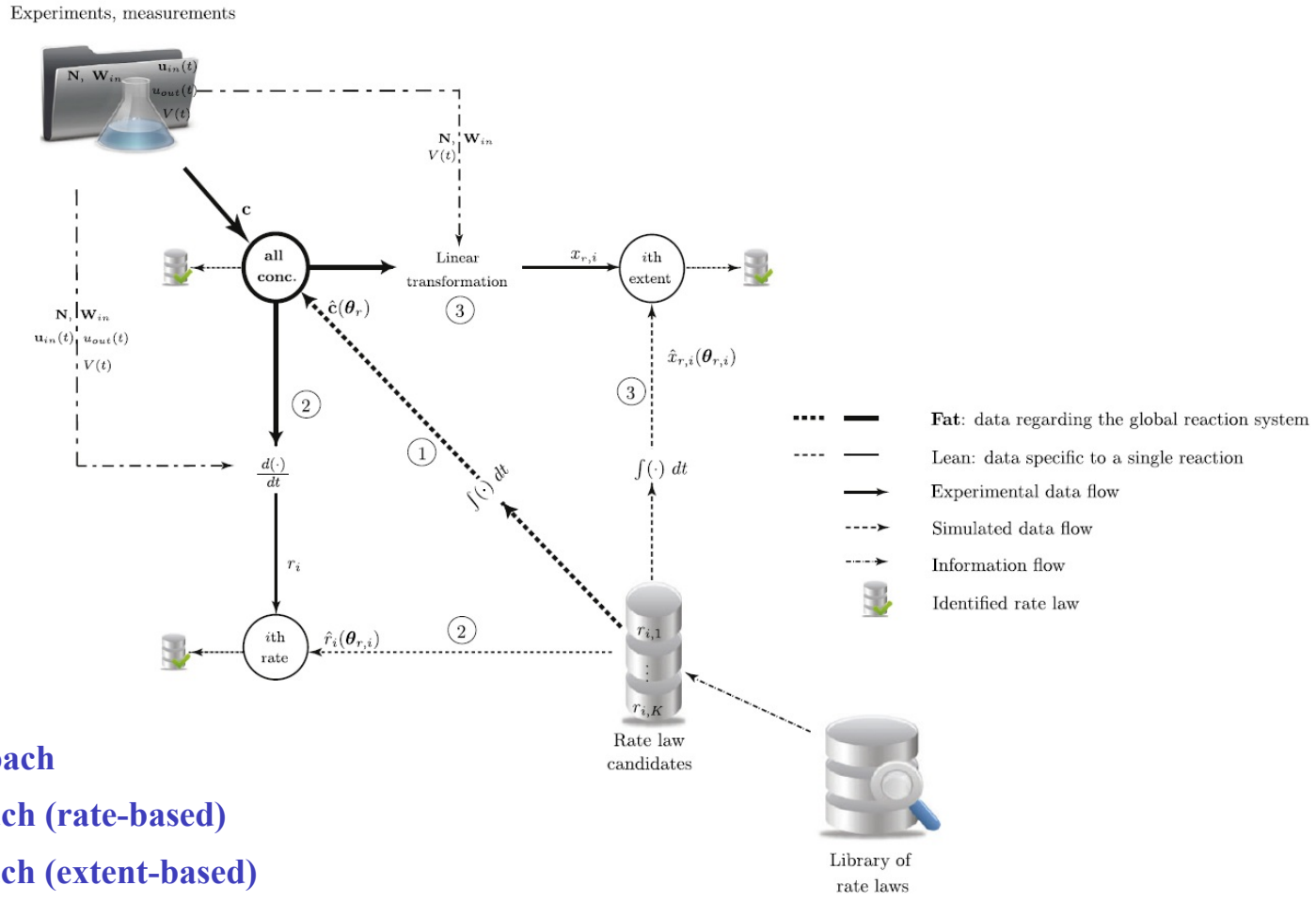
Kinetic investigation
From measurements to rate expressions



① **Simultaneous approach**

② **Incremental approach (rate-based)**

③ **Incremental approach (extent-based)**

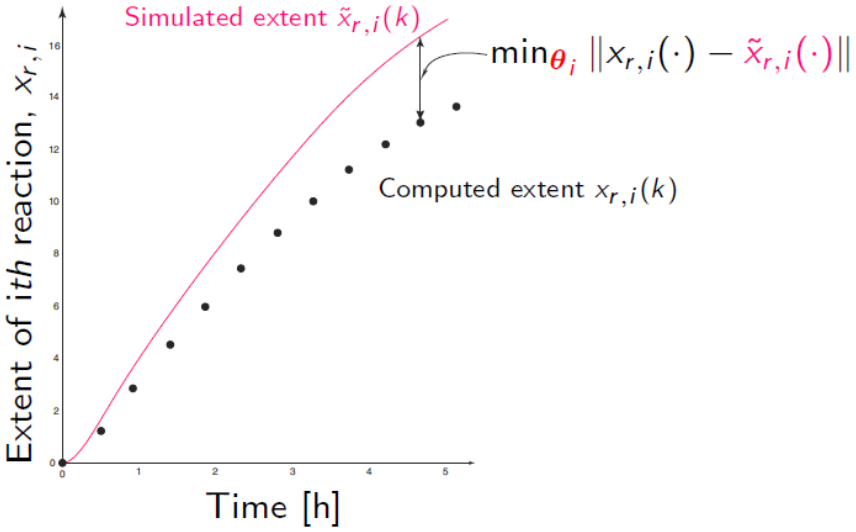
Incremental model identification
Extent-based method

- The kinetic problem is decomposed into sub-problems of lower complexity that are solved individually.
- The model identification proceeds in **two steps**:
  - **Transformation to extents (v+iv)**
    Computation of the contribution of each dynamic effect (reaction, inlets and outlets) as *extents*
  - **Model identification (Parameter estimation)**
    Individual model identification of each effect from its corresponding *extent* with the integral method of parameter estimation.

Extent-based model identification
Model identification and parameter estimation

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of *R* extents of reaction



Extent-based model identification
Model identification and parameter estimation

A dynamic model is postulated for each extent of interest and a regression problem is solved individually using the integral method of parameter estimation.

Example: fitting of R extents of reaction

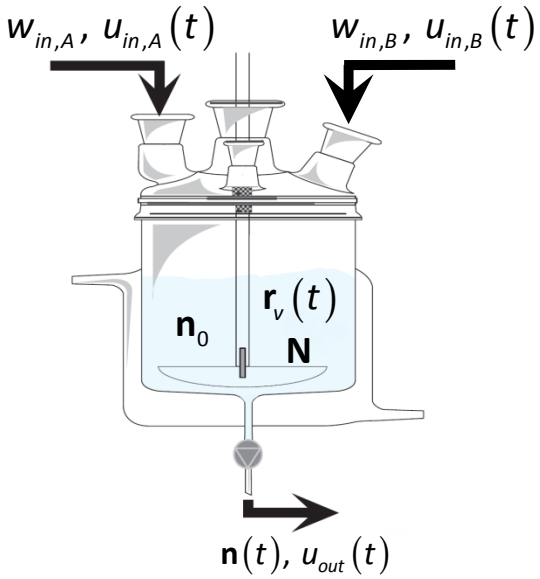
$$\min_{\boldsymbol{\theta}_{r,i}} \left\| x_{r,i}(t) - \hat{x}_{r,i}\left(t, \boldsymbol{\theta}_{r,i}\right) \right\|^2 \qquad i = 1, \ \ldots, \ R$$

$$\text{s.t.} \quad \dot{\hat{x}}_{r,i}\left(t, \boldsymbol{\theta}_{r,i}\right) = r_{v,i}\left(t, \boldsymbol{\theta}_{r,i}\right) - \frac{u_{out}(t)}{m(t)} \hat{x}_{r,i}(t), \qquad \hat{x}_{r,i}(0) = 0$$

$$\boldsymbol{\theta}_{r,i}^{L} \le \boldsymbol{\theta}_{r,i} \le \boldsymbol{\theta}_{r,i}^{U}$$

Homogeneous reaction systems
Ethanolysis of phthalyl chloride in a CSTR

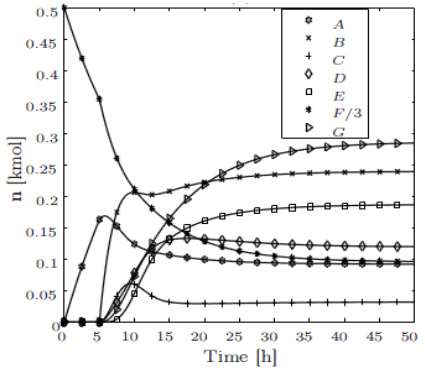
Ethanolysis of phthalyl chloride (A) comprising seven species ($S = 7$), three reactions ($R = 3$), two inlets ($p = 2$) and 1 outlet



$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 1 & 1 \end{bmatrix}$$

$$\mathbf{W}_{in} = \begin{bmatrix} w_{in,A} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & w_{in,B} & 0 & 0 & 0 & 0 & 0 \end{bmatrix}^T$$

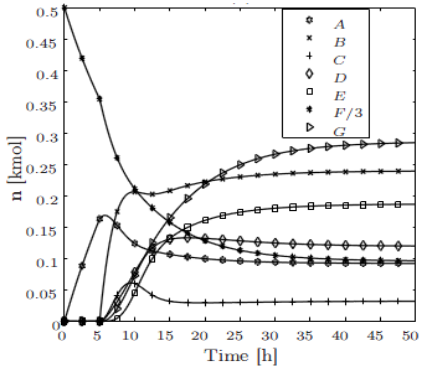
$$A + B \rightarrow C + D$$
$$C + B \rightarrow E + D$$
$$D + B \rightleftarrows F + G$$



Extents of reaction ?

Homogeneous reaction systems
Ethanolysis of phthalyl chloride in a CSTR

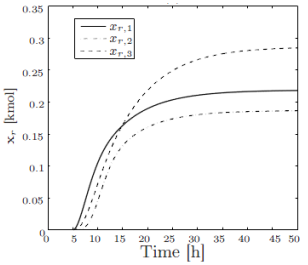
Number of moles



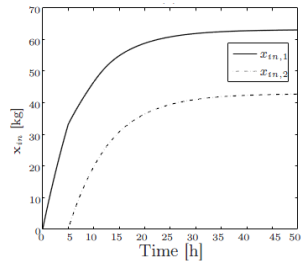
$\mathbf{N}, \mathbf{W}_{in}, \mathbf{n}_0$

$$\mathscr{L} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{q}^{\mathrm{T}} \\ \mathbf{Q} \end{bmatrix}$$

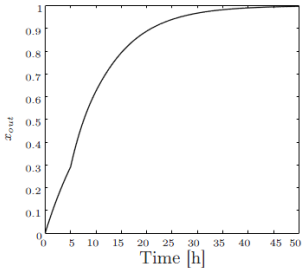
$R = 3$ **Extents of reaction**



$p = 2$ Extents of inlet



1 Extents of outlet



Each extent of reaction can then be modeled individually, that is, independently from all the other phenomena / extents…

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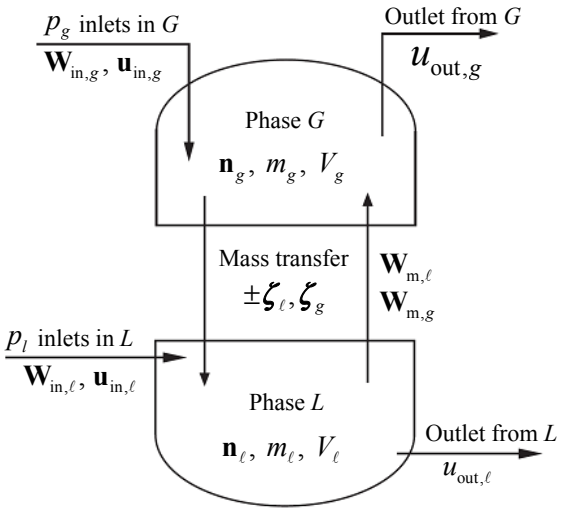
- ○ **Fluid-Fluid reaction systems**
- ○ Extensions to calorimetry and spectroscopy
- ○ Perspectives: distributed reaction systems

Fluid-Fluid reaction systems
Mole balance equations

Fluid-Fluid reaction system consisting of:

- **Phase *L***: S_ℓ species with R_ℓ reactions, p_m mass transfers, p_ℓ inlets and 1 outlet
- **Phase *G***: S_g species with R_g reactions, p_m mass transfers, p_g inlets and 1 outlet

Mass transfer described by various models…



Mole balances on phase B

R_b reactions, p_{m} mass transfers, p_b inlets, 1 outlet

$$B \in \{L, G\},\ b \in \{\ell, g\}$$

$$\dot{\mathbf{n}}_b(t) = \mathbf{N}_b^{\mathrm{T}}\mathbf{r}_{v,b}(t) \pm \mathbf{W}_{m,b}\boldsymbol{\zeta}_b(t) + \mathbf{W}_{in,b}\mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)}\mathbf{n}_b(t), \qquad \mathbf{n}_b(0) = \mathbf{n}_{0,b}$$

$(S_b \times 1)$ $(S_b \times R_b)(R_b \times 1)$ $(S_b \times p_m)(p_m \times 1)$ $(S_b \times p_b)(p_b \times 1)$ $(S_b \times 1)$

Fluid-Fluid reaction systems
Decomposition in variants and invariants

- Condition: $\operatorname{rank}\left(\left[\mathbf{N}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}\ \mathbf{W}_{in,b}\ \mathbf{n}_{0,b}\right]\right) = R_b + p_m + p_b + 1$

$$\begin{bmatrix}\mathbf{x}_r(t)\\ \mathbf{x}_m(t)\\ \mathbf{x}_{in}(t)\\ x_{ic}(t)\\ \mathbf{x}_{iv}(t)\end{bmatrix} \overset{\mathscr{L}_b}{=} \begin{bmatrix}\mathbf{R}_b\\ \mathbf{M}_b\\ \mathbf{F}_b\\ \mathbf{q}_b^{\mathrm{T}}\\ \mathbf{Q}_b\end{bmatrix} \left(\mathbf{n}_b(t) - \mathbf{n}_{0,b}\right) \qquad b \in \{\ell, g\}$$

- Vessel extents (variants) and $q_b = S_b - R_b - p_m - p_b - 1$ invariants

$$\dot{\mathbf{x}}_{r,b}(t) = \underbrace{\mathbf{R}_b\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{I}_{R_b}}\mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{R}_b\ \mathbf{W}_{m,b}}_{\mathbf{0}_{R_b\times p_m}}\boldsymbol{\zeta}_b(t) + \underbrace{\mathbf{R}_b\ \mathbf{W}_{in,b}}_{\mathbf{0}_{R_b\times p_b}}\mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)}\mathbf{x}_{r,b}(t), \qquad \mathbf{x}_{r,b}(0) = \mathbf{0}_{R_b}$$

$$\dot{\mathbf{x}}_{m,b}(t) = \underbrace{\mathbf{M}_b\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}_{p_m\times R_b}}\mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{M}_b\ \mathbf{W}_{m,b}}_{\mathbf{I}_{p_m}}\boldsymbol{\zeta}_b(t) + \underbrace{\mathbf{M}_b\ \mathbf{W}_{in,b}}_{\mathbf{0}_{p_m\times p_b}}\mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)}\mathbf{x}_{m,b}(t), \qquad \mathbf{x}_{in,b}(0) = \mathbf{0}_{p_m}$$

$$\dot{\mathbf{x}}_{in,b}(t) = \underbrace{\mathbf{F}_b\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}_{p_b\times R}}\mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{F}_b\ \mathbf{W}_{m,b}}_{\mathbf{0}_{p_b\times p_m}}\boldsymbol{\zeta}_b(t) + \underbrace{\mathbf{F}_b\ \mathbf{W}_{in}}_{\mathbf{I}_{p_b}}\mathbf{u}_{in,b}(t) - \frac{u_{out}(t)}{m_b(t)}\mathbf{x}_{in,b}(t), \qquad \mathbf{x}_{in,b}(0) = \mathbf{0}_{p_b}$$

$$\dot{x}_{ic,b}(t) = \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{N}_b^{\mathrm{T}}}_{\mathbf{0}_{1\times R_b}}\mathbf{r}_{v,b}(t) \pm \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{W}_{m,b}}_{\mathbf{0}_{1\times p_m}}\boldsymbol{\zeta}_b(t) + \underbrace{\mathbf{q}_b^{\mathrm{T}}\ \mathbf{W}_{in,b}}_{\mathbf{0}_{1\times p_b}}\mathbf{u}_{in,b}(t) - \frac{u_{out,b}(t)}{m_b(t)}\left(1 + x_{ic,b}(t)\right), \qquad x_{ic,b}(0) = 0$$

Fluid-Fluid reaction systems
Decomposition in variants and invariants

- Condition: $\operatorname{rank}\left(\left[\mathbf{N}_b^{\mathrm{T}} \;\; \mathbf{W}_{m,b} \;\; \mathbf{W}_{in,b} \;\; \mathbf{n}_{0,b}\right]\right) = R_b + p_m + p_b + 1$

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_m(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} \overset{\mathscr{L}_b}{=} \begin{bmatrix} \mathbf{R}_b \\ \mathbf{M}_b \\ \mathbf{F}_b \\ \mathbf{q}_b \\ \mathbf{Q}_b \end{bmatrix} \left(\mathbf{n}_b(t) - \mathbf{n}_{0,b}\right) \qquad b \in \{\ell, g\}$$

- Vessel extents (variants) and $q_b = S_b - R_b - p_m - p_b - 1$ invariants

$$\begin{aligned}
\dot{\mathbf{x}}_{r,b}(t) &= \mathbf{r}_{v,b}(t) - \tfrac{u_{out,b}(t)}{m_b(t)}\mathbf{x}_{r,b}(t), & \mathbf{x}_{r,b}(0) &= \mathbf{0}_{R_b} \\
\dot{\mathbf{x}}_{m,b}(t) &= \boldsymbol{\zeta}_b(t) - \tfrac{u_{out,b}(t)}{m_b(t)}\mathbf{x}_{m,b}(t), & \mathbf{x}_{in,b}(0) &= \mathbf{0}_{p_m} \\
\dot{\mathbf{x}}_{in,b}(t) &= \mathbf{u}_{in,b}(t) - \tfrac{u_{out}(t)}{m_b(t)}\mathbf{x}_{in,b}(t), & \mathbf{x}_{in,b}(0) &= \mathbf{0}_{p_b} \\
\dot{x}_{ic,b}(t) &= -\tfrac{u_{out,b}(t)}{m_b(t)} - \tfrac{u_{out,b}(t)}{m_b(t)}x_{ic,b}(t), & x_{ic,b}(0) &= 0 \qquad \text{with } \mathbf{x}_{iv,b}(t) = \mathbf{0}_{q_b}
\end{aligned}$$

$$\left(\mathbf{n}_b(t) - \mathbf{n}_{0,b}\right) \overset{\mathscr{L}_b^{-1}}{=} \mathbf{N}_b^{\mathrm{T}}\mathbf{x}_{r,b}(t) \pm \mathbf{W}_{m,b}\mathbf{x}_{m,b}(t) + \mathbf{W}_{in,b}\mathbf{x}_{in,b}(t) + \mathbf{n}_{0,b}x_{ic,b}(t)$$

Fluid-Fluid reaction systems

Orthogonal spaces in 5-way decomposition

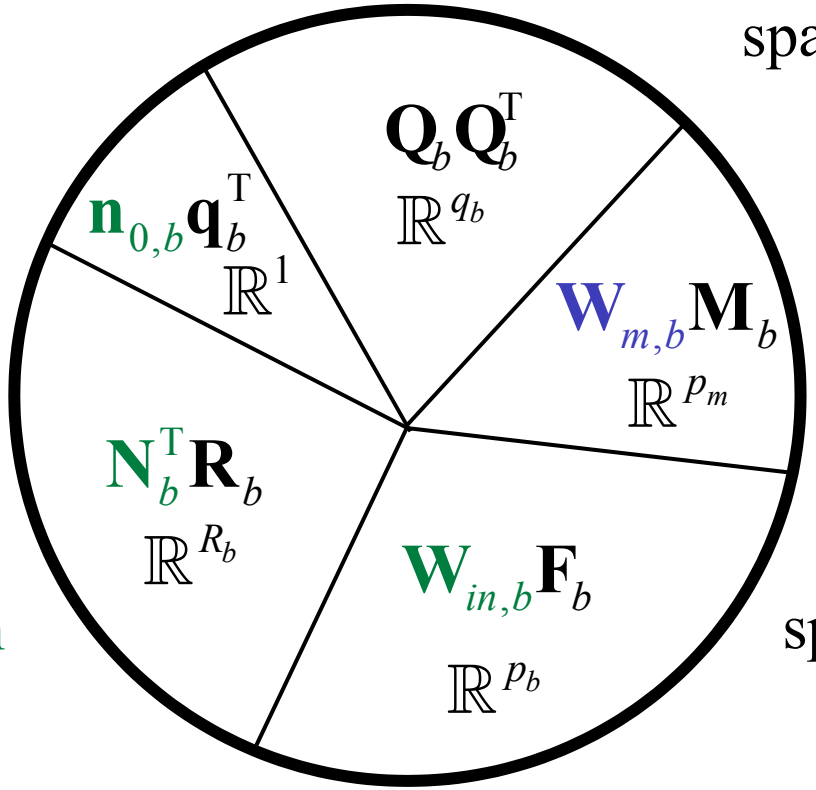
space of initial conditions

space of invariants

space of mass-transfer extents

space of reaction extents

space of inlet extents



S_b-dim space of the number of moles in phase *B*

Fluid-Fluid reaction systems
Transformation to RMV form

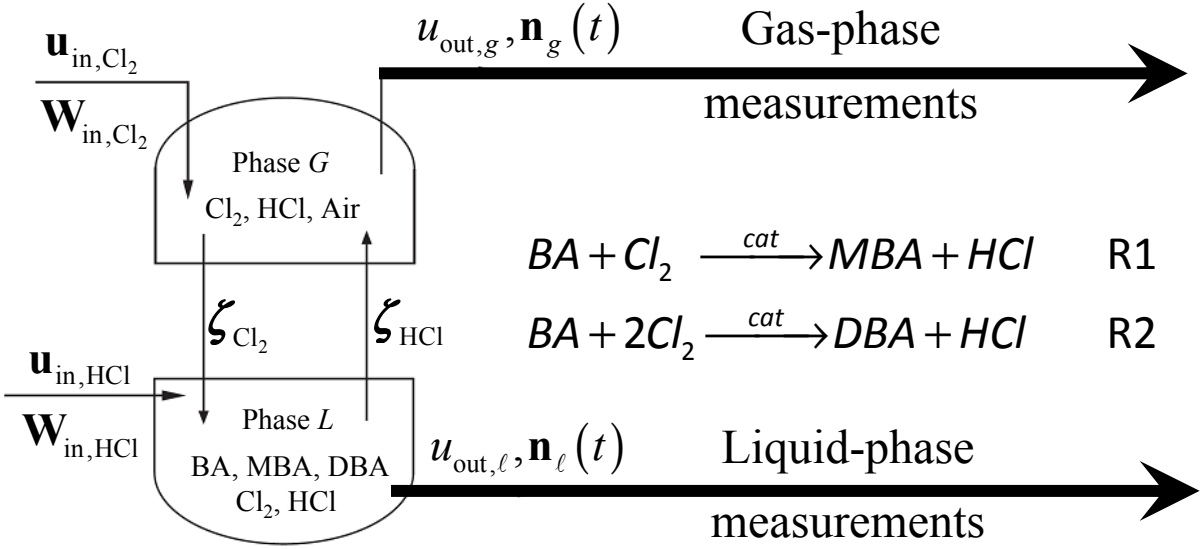
- When $\text{rank}\left(\left[\mathbf{N}_b^{\mathrm{T}} \;\; \mathbf{W}_{m,b} \;\; \mathbf{W}_{in,b} \;\; \mathbf{n}_{0,b}\right]\right) < R_b + p_m + p_b + 1$ $\left(\mathbf{u}_{in,b}(t) \text{ and } u_{out,b}(t) \text{ known}\right)$, the numbers of moles are rearranged in **R**eaction **M**ass-transfer **V**ariant (RMV) form:

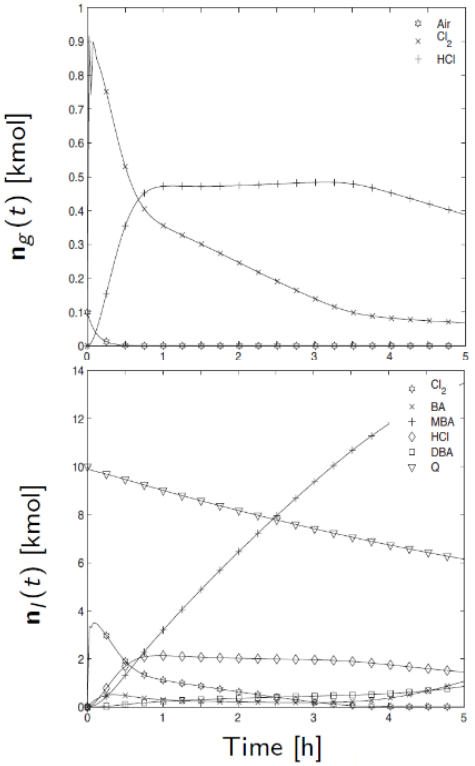
$$\mathbf{n}_b^{\mathrm{RMV}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_{r,b}(t) \pm \mathbf{W}_{m,b}\mathbf{x}_{m,b}(t) = \left[\mathbf{N}^{\mathrm{T}} \;\; \pm\mathbf{W}_{m,b}\right]\begin{bmatrix}\mathbf{x}_{r,b}(t)\\ \mathbf{x}_{m,b}(t)\end{bmatrix}$$
$$= \mathbf{n}_b(t) - \mathbf{W}_{in,b}\mathbf{x}_{in,b}(t) - \mathbf{n}_{0,b}\left(1 + x_{ic,b}(t)\right)$$

- The R_b **vessel extents of reaction** and p_m **extents of mass transfer** are then computed as: $\begin{bmatrix}\mathbf{x}_{r,b}(t)\\ \mathbf{x}_{m,b}(t)\end{bmatrix} = \left[\mathbf{N}^{\mathrm{T}} \;\; \pm\mathbf{W}_{m,b}\right]^{+}\mathbf{n}_b^{\mathrm{RMV}}(t)$

Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

Chlorination of butanoic acid comprises $S_\ell = 5$ (BA, MBA, DBA, Cl_2, HCl) and $S_g = 3$ (Cl_2, HCl, air) species, $R_\ell = 2$ reactions, $p_\ell = 1$ and $p_g = 1$ inlets and 2 outlets





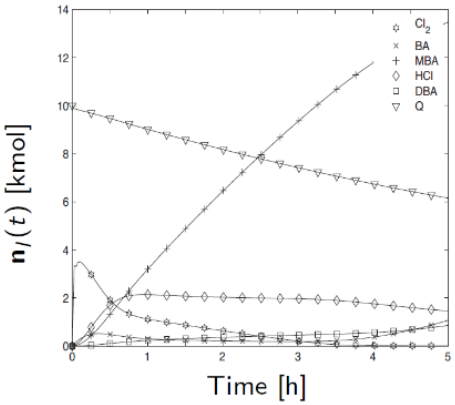
Extents of reaction ?

Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

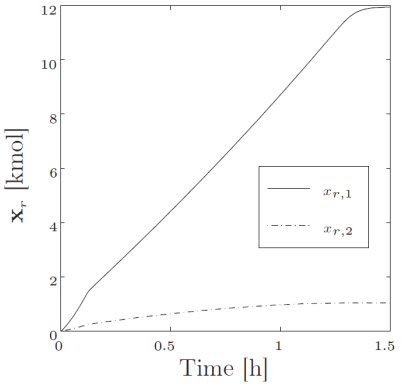
$R = 2$ **Extents of reaction**

$\mathbf{N}_\ell$, $\mathbf{W}_{m,\ell}$, $\mathbf{W}_{in,\ell}$, $\mathbf{n}_{0,\ell}$

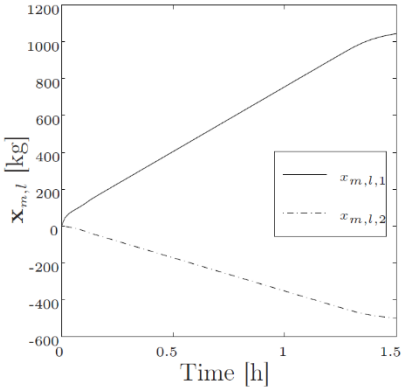
Number of moles in liquid phase



$$\mathscr{L}_\ell = \begin{bmatrix} \mathbf{R}_\ell \\ \mathbf{M}_\ell \\ \mathbf{f}_\ell \\ \mathbf{q}_\ell^{\mathrm{T}} \\ \mathbf{Q}_\ell \end{bmatrix}$$



$p_m = 2$ Extents of m.t.



Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

- Identification of the rate expression for the main reaction R1
- Rate expression candidates

$$r_1^{(1)} = k_1 \; c_{\ell,\mathrm{BA}} \; c_{\ell,\mathrm{Cl_2}}$$

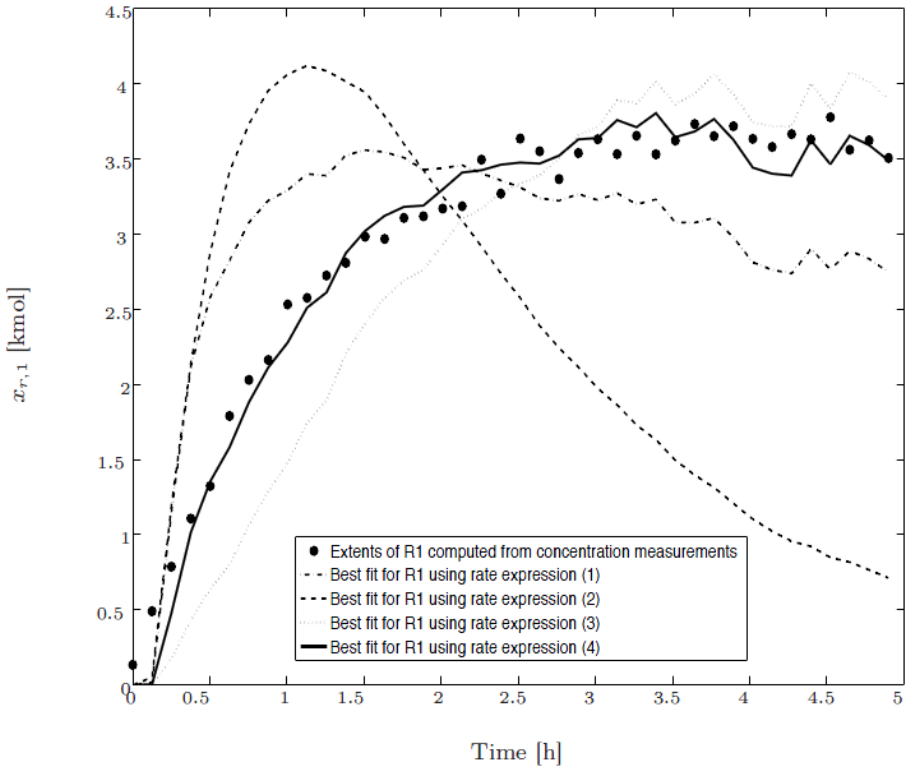
$$r_1^{(2)} = k_1 \; c_{\ell,\mathrm{Cl_2}}$$

$$r_1^{(3)} = k_1 \; c_{\ell,\mathrm{BA}} \; c_{\ell,\mathrm{Cl_2}} \; c_{\ell,\mathrm{MBA}}$$

$$r_1^{(4)} = k_1 \; c_{\ell,\mathrm{BA}} \; c_{\ell,\mathrm{Cl_2}} \; \sqrt{c_{\ell,\mathrm{MBA}}}$$

- Identified rate expression

$$r_1^{(4)} = 1.3543 \; c_{\ell,\mathrm{BA}} \; c_{\ell,\mathrm{Cl_2}} \; \sqrt{c_{\ell,\mathrm{MBA}}}$$



Fluid-Fluid reaction systems
Chlorination of butanoic acid in a CSTR

- Identified rate expressions

$$r_1 = k_1 \; c_{\ell,\mathrm{BA}} \; c_{\ell,\mathrm{Cl_2}} \; \sqrt{c_{\ell,\mathrm{MBA}}}$$

$$r_2 = k_2 \; r_1 \; c_{\ell,\mathrm{Cl_2}}$$

$$\zeta_{\mathrm{Cl_2}} = k_{\mathrm{Cl_2}} \; A_s \; V_\ell \; M_{w,\mathrm{Cl_2}} \left(c^*_{\mathrm{Cl_2}} - c_{\ell,\mathrm{Cl_2}} \right)$$

$$\zeta_{\mathrm{HCl}} = k_{\mathrm{HCl}} \; A_s \; V_\ell \; M_{w,\mathrm{HCl}} \left(c_{\ell,\mathrm{HCl}} - c^*_{\mathrm{HCl}} \right)$$

- Results of curve fitting (2% noise level)

Parameter	Simulated value	Estimated value	95% Confidence interval
k_1	1.3577	1.3543	[1.3207 – 1.3879]
k_2	0.1	0.105	[0.0884 – 0.1216]
$k_{\mathrm{Cl_2}}$	$0.666 \cdot 10^{-4}$	$0.594 \cdot 10^{-4}$	$[0.514 \cdot 10^{-4} – 0.674 \cdot 10^{-4}]$
k_{HCl}	$0.845 \cdot 10^{-4}$	$0.813 \cdot 10^{-4}$	$[0.763 \cdot 10^{-4} – 0.863 \cdot 10^{-4}]$

Outline

- ✓ Motivation
- ✓ Concept of vessel extent
- ✓ Homogeneous reaction systems
- ✓ Incremental model identification
- ✓ Fluid-Fluid reaction systems
- ○ **Extensions to calorimetry and spectroscopy**
- ○ Perspectives: distributed reaction systems

Recent extensions
Rank augmentation of conc. data by calorimetry

- Homogeneous reaction systems

$$\mathbf{n}_{aug}^{\mathrm{RV}}(t) := \begin{bmatrix} \mathbf{n}_{a}^{\mathrm{RV}}(t) \\ Q_r(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_{a}^{\mathrm{T}} \\ -\Delta\mathbf{H}_{r}^{\mathrm{T}} \end{bmatrix} \mathbf{x}_r(t) := \mathbf{N}_{aug}^{\mathrm{T}} \mathbf{x}_r(t)$$

$$\mathbf{x}_r(t) = \left(\mathbf{N}_{aug}^{\mathrm{T}}\right)^{+} \mathbf{n}_{aug}^{\mathrm{RV}}(t)$$

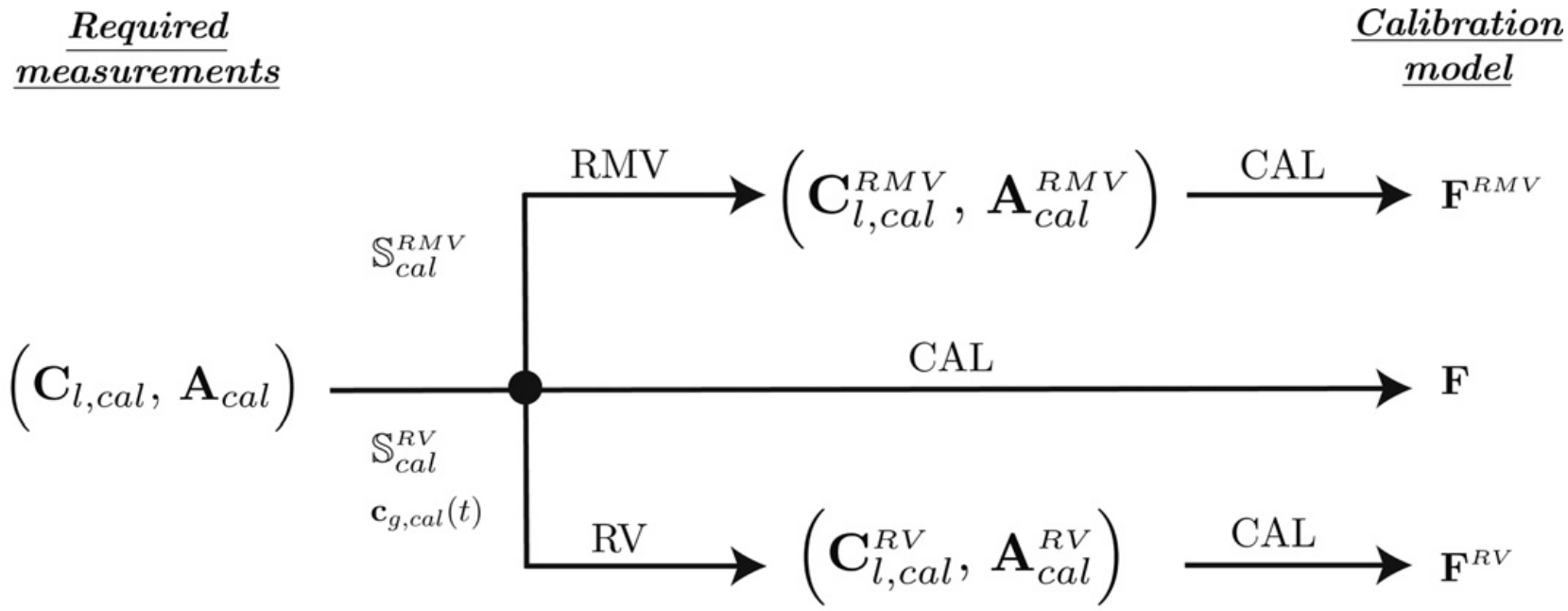
- Fluid-Fluid reaction systems

$$\mathbf{n}_{aug}^{\mathrm{RMV}}(t) := \begin{bmatrix} \mathbf{n}_{\ell,a}^{\mathrm{RMV}}(t) \\ Q_{rm}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{N}_{\ell,a}^{\mathrm{T}} & \mathbf{W}_{m,\ell,a} \\ -\Delta\mathbf{H}_{r,\ell}^{\mathrm{T}} & -\Delta\mathbf{H}_{m,\ell}^{\mathrm{T}} \end{bmatrix} \begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix} := \mathbf{N}_{\ell,aug}^{\mathrm{T}} \begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix}$$

$$\begin{bmatrix} \mathbf{x}_{r,\ell}(t) \\ \mathbf{x}_{m,\ell}(t) \end{bmatrix} = \left(\mathbf{N}_{\ell,aug}^{\mathrm{T}}\right)^{+} \mathbf{n}_{aug}^{\mathrm{RMV}}(t)$$

Recent extensions

Construction of calibration models in spectroscopy



RMV, RV : transformation to RMV-, RV-form

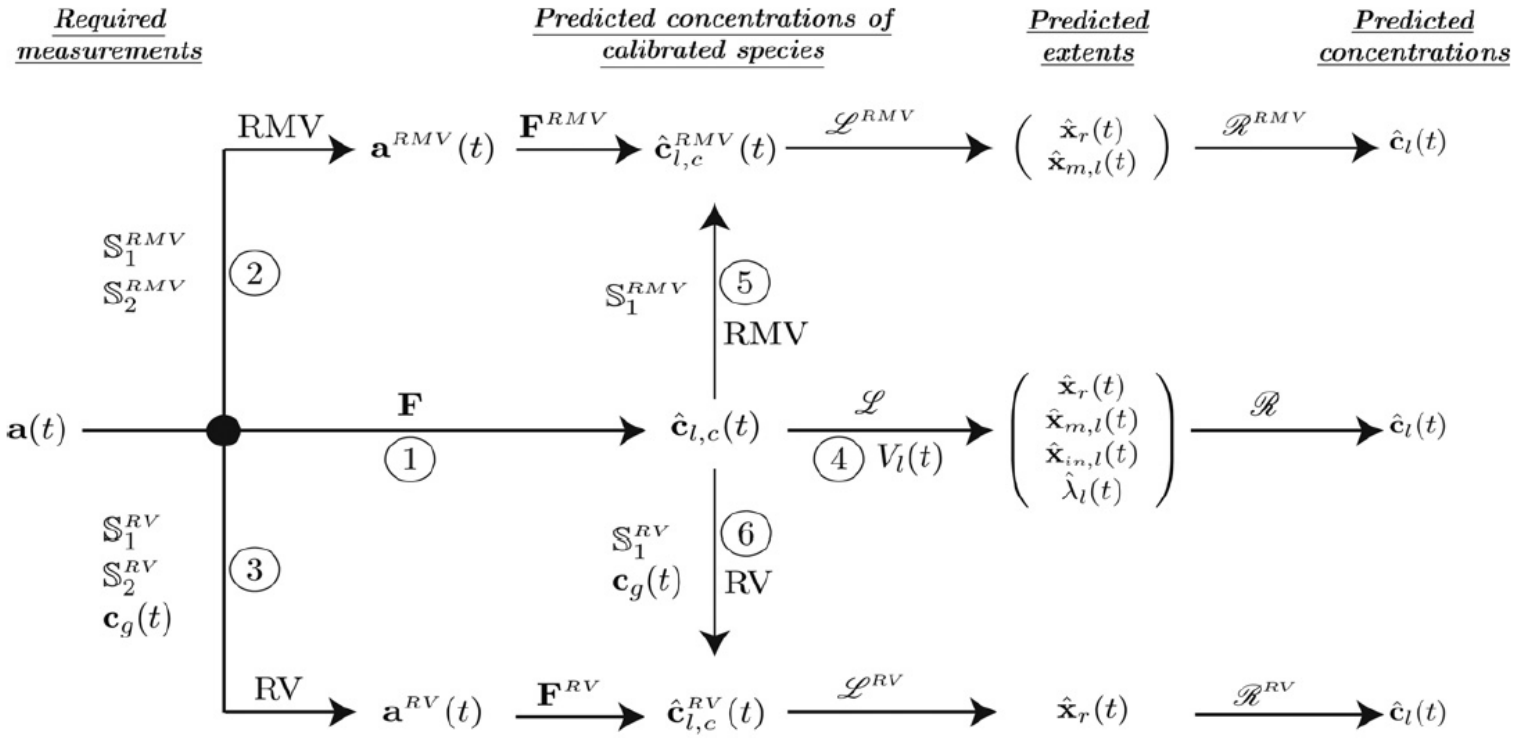
CAL : construction of calibration model

$\mathbb{S}_{cal}^{RMV} = \{\mathbf{u}_{in,l,cal}(t),\ u_{out,l,cal}(t),\ m_{l,cal}(t),\ V_{l,cal}(t),\ \mathbf{W}_{in,l,cal},\ \mathbf{n}_{l0,cal},\ \mathbf{A}_{in,cal},\ \mathbf{a}_{0,cal}\}$

$\mathbb{S}_{cal}^{RV} = \{\mathbf{u}_{in,f,cal}(t),\ u_{out,f,cal}(t),\ m_{f,cal}(t),\ V_{f,cal}(t),\ \mathbf{W}_{in,f,cal},\ \mathbf{W}_{m,f,cal},\ \mathbf{n}_{f0,cal},\ \mathbf{A}_{in,cal},\ \mathbf{a}_{0,cal},\ \mathbf{A}_{m,cal}\}$

Recent extensions

Prediction of concentrations from spectral data

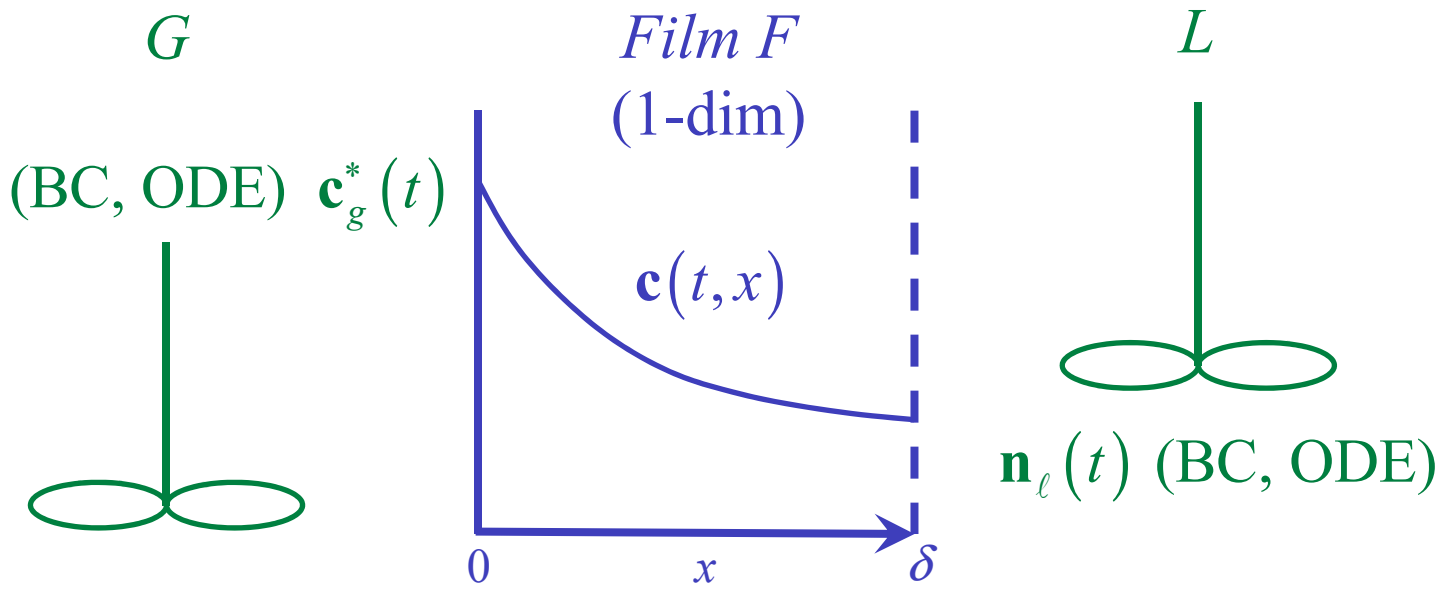


$\mathbf{F}, \mathbf{F}^{RV}, \mathbf{F}^{RMV}$	: prediction via calibration	$\mathbb{S}_1^{RMV} = \{\mathbf{u}_{in,l}(t), u_{out,l}(t), m_l(t), V_l(t), \mathbf{W}_{in,l}, \mathbf{n}_{l0}\}$
$\mathscr{L}, \mathscr{L}^{RV}, \mathscr{L}^{RMV}$	: linear transformation to extents	$\mathbb{S}_2^{RMV} = \{\mathbf{A}_{in}, \mathbf{a}_0\}$
$\mathscr{R}, \mathscr{R}^{RV}, \mathscr{R}^{RMV}$	: reconstruction of all concentrations from extents	$\mathbb{S}_1^{RV} = \{\mathbf{u}_{in,f}(t), u_{out,f}(t), m_f(t), V_f(t), \mathbf{W}_{in,f}, \mathbf{W}_{m,f}, \mathbf{n}_{f0}\}$, where $f \in \{g,l\}$
RMV, RV	: transformation to RMV-, RV-form	$\mathbb{S}_2^{RV} = \{\mathbf{A}_{in}, \mathbf{A}_m, \mathbf{a}_0\}$

Outline

- ✓ Motivation
- ✓ Concept of vessel extent
- ✓ Homogeneous reaction systems
- ✓ Incremental model identification
- ✓ Fluid-Fluid reaction systems
- ✓ Extensions to calorimetry and spectroscopy
- ○ **Perspectives: distributed reaction systems**

Perspectives
Distributed reaction systems



PDE: $\frac{d}{dt}\mathbf{c}(t,x) = \mathbf{N}^{\mathrm{T}}\mathbf{r}(t,x) + \mathbf{D}\frac{d^2}{dx^2}\mathbf{c}(t,x),$

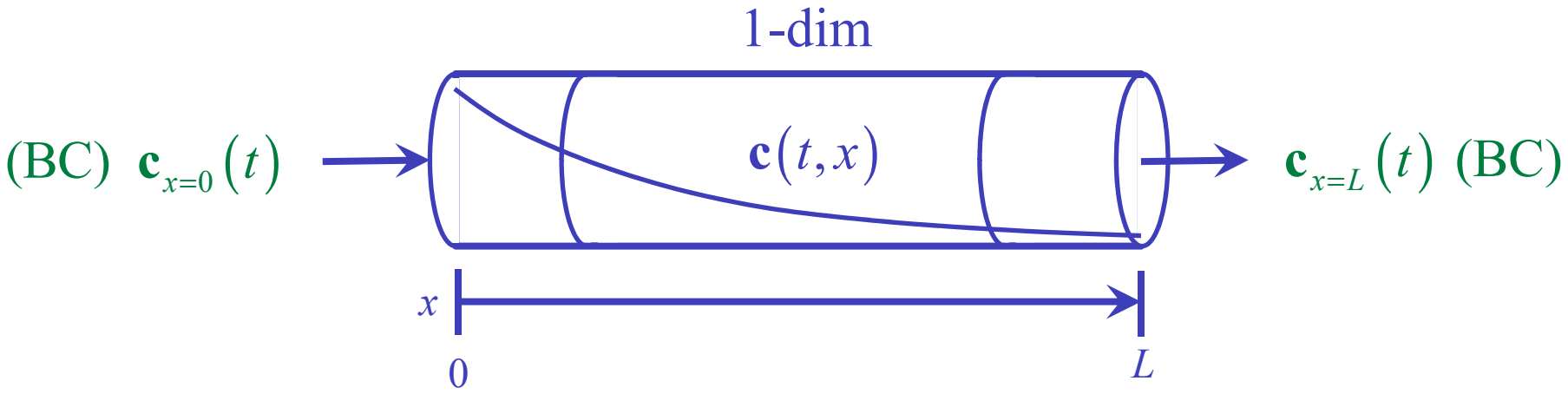
How to decouple reaction and diffusion phenomena?

$\mathbf{c}(0,x) = \mathbf{c}_0(x)$ (IC)

$\mathbf{c}(t,0) = \mathbf{c}_g^*(t)$ (BC)

$\mathbf{c}(t,\delta) = \frac{\mathbf{n}_\ell(t)}{V_\ell(t)}$ (BC)

Perspectives
Distributed reaction systems



PDE: $\frac{d}{dt}\mathbf{c}(t,x) = \mathbf{N}^{\mathrm{T}}\mathbf{r}(t,x) - v_x \frac{d}{dx}\mathbf{c}(t,x) + \mathbf{D}\frac{d^2}{dx^2}\mathbf{c}(t,x),$

$\mathbf{c}(0,x) = \mathbf{c}_{t=0}(x)$ (IC)

$\mathbf{c}(t,0) = \mathbf{c}_{x=0}(t)$ (BC)

$\mathbf{c}(t,\delta) = c_{x=L}(t)$ (BC)

How to decouple reaction, convection and diffusion phenomena?

Laboratoire d'Automatique

Prof. Bonvin, Prof. Longchamp, Prof. Jones, Dr. MER Karimi

6 Postdocs + 20 PhD students + technical / administrative staff

Thank you for your attention

Model reduction

- M. Amrhein, PhD dissertation n°1861 (1998), EPFL, Switzerland
- Bhatt et al, Comp. & Chem. Eng. (2011), submitted

Transformation to variants/invariants (extents)

- N. Bhatt, PhD dissertation n°5028 (2011), EPFL, Switzerland
- Amrhein et al, AIChE J. 56 (2010) 2873
- Bonvin et al, TFMST, Lyon, July 13–16, 2013 (to be published)

Incremental model identification

- Bhatt et al, Ind. & Eng. Chem. Res. 49 (2010) 7704
- Bhatt et al, Ind. & Eng. Chem. Res. 50 (2011) 12960
- Bhatt et al, Chem. Eng. Sci. 8 (2012) 24

Rank augmentation by calorimetric data

- Srinivasan et al, Chem. Eng. J. 207-208 (2012) 785

Incremental kinetic modeling of spectroscopic data

- Billeter et al, Anal. Chim. Acta 767 (2013) 21